

AD-A209 561

2

OFFICE OF NAVAL RESEARCH

Contract N00014-79-C-0647

TECHNICAL REPORT #50

A Study of Non-Rigid Aromatic Molecules by Supersonic Molecular
Jet Spectroscopy: Observation and Spectroscopic Analysis of the
Stable Conformations of Various Alkylbenzenes

by

J. I. Seeman, H. V. Secor, P. J. Breen, V. H. Grassian and E.R. Bernstein

Prepared for Publication

in the

Journal of Physical Chemistry

DTIC
ELECTE
JUN 23 1989
S D & D

Department of Chemistry
Colorado State University
Fort Collins, Colorado 80523

June 1, 1989

Reproduction in whole or in part is permitted for
any purpose of the United States Government.

This document has been approved for public release
and sale; its distribution is unlimited

89 6 17

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
1a REPORT SECURITY CLASSIFICATION			1b RESTRICTIVE MARKINGS		
2a SECURITY CLASSIFICATION AUTHORITY			3 DISTRIBUTION AVAILABILITY OF REPORT Approved for public release; distribution unlimited.		
2b DECLASSIFICATION/DOWNGRADING SCHEDULE Unclassified			5 MONITORING ORGANIZATION REPORT NUMBER(S)		
4 PERFORMING ORGANIZATION REPORT NUMBER(S) N00014-79-C-0647			7a NAME OF MONITORING ORGANIZATION		
6a NAME OF PERFORMING ORGANIZATION Colorado State University		6b OFFICE SYMBOL (if applicable)	7b ADDRESS (City, State, and ZIP Code)		
6c ADDRESS (City, State, and ZIP Code) Department of Chemistry Fort Collins, CO 80523		9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-79-C-0647			
8a NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research		8b OFFICE SYMBOL (if applicable)	10 SOURCE OF FUNDING NUMBERS		
8c ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217-5000		PROGRAM ELEMENT NO	PROJECT NO	TASK NO	ACCESSION NO
11 TITLE (Include Security Classification) "A Study of Non-Rigid Aromatic Molecules by Supersonic Molecular Jet Spectroscopy: Observation and Soectroscopic Analysis of the Stable Conformations of Various Alkylbenzenes."					
12 PERSONAL AUTHOR(S) J. I. Seeman, H. V. Secor, P.J. Breen, V. H. Grassian and E. R. Bernstein					
13a TYPE OF REPORT Technical Report		13b TIME COVERED FROM _____ TO _____		14 DATE OF REPORT (Year Month Day) June 1, 1989	
16 SUPPLEMENTARY NOTATION					
17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB GROUP	non rigid molecules, alkyl benzene, structure of substituted benzenes, supersonic jet, conformers of aromatic molecules, conformations		
19 ABSTRACT (Continue on reverse if necessary and identify by block number) SEE ATTACHED ABSTRACT					
20 DISTRIBUTION AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> OTIC USERS			21 ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a NAME OF RESPONSIBLE INDIVIDUAL Elliot R. Bernstein			22b TELEPHONE (Include Area Code) (303) 491-6347		22c OFFICE SYMBOL

DD Form 1473, JUN 86

Previous editions are obsolete

S/N 0102-LF-014-6603

SECURITY CLASSIFICATION OF THIS PAGE

ABSTRACT

The technique of supersonic molecular jet laser spectroscopy was used to determine the stable conformations of a series of alkylbenzenes. This study demonstrates, for the first time, the sensitivity of molecular jet spectroscopy in determining both the number of stable conformations as well as the geometry of various ethyl, propyl, and butyl substituents relative to the aromatic ring. Different rotamers with low barriers to interconversion, >5 kcal/mol. can be isolated in the supersonic jet expansion. Each observed conformation exhibits its own spectroscopic origin ($S_1 \leftarrow S_0$ transition) in a two-color time-of-flight mass spectrum (TOFMS). The number of stable conformations is then used to determine the minimum energy geometries of the substituent group. Previous identification of individual molecular conformations for such low barriers to interconversion has not been attainable with conventional techniques such as variable-temperature NMR.

Accession For	
NTIS CHAS1	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution	
Availability Codes	
Dist	Availability for Special
A-1	



TTL03

SEN03

SEN06 4

ADR03 2

ALT03

ALT09

AAS03

RCV01 15

ABS03

SEN00

SEN06 15

SEN09 17

SEN12 17

SEN15 15

SEN18 6

SEN19 4

TXT03

PAR03

SEN03

SEN06 20

SEN09 4

SEN09 1

SEN12 2

SEN12 11

SEN12 4

SEN12 19

SEN12 27

PAR06

SEN03

SEN06 21

SEN06 22

SEN09 24

SEN09 35

SEN09 36

PAR09

SEN03

SEN06 1

SEN09 6

SEN09 17

SEN09 6

SEN12 25

SEN12 0

SEN15 1

SEN15 20

PAR12

SEN03

SEN06 14

SEN06 34

SEN06 9

SEN09 29

SEN09 41

SEN09 54

SEN09 65

SEN09 28

SEN09 41

PAR15

SEN03

SEN06 0

SEN06 27

SEN06 29

SEN06 36

A Study of Nonrigid Aromatic Molecules. Observation and Spectroscopic Analysis of the Stable Conformations of Various Alkylbenzenes by Supersonic Molecular Jet Laser Spectroscopy

Jeffrey I. Seeman,^{a,1a} Henry V. Secor,^{1a} P. J. Breen,^{1b,c} V. H. Grassian,^{1b} and E. R. Bernstein^{a,1b}

Contribution from the Philip Morris Research Center, P.O. Box 26583, Richmond, Virginia 23261, and the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523. Received April 26, 1988

Abstract: The technique of supersonic molecular jet laser spectroscopy was used to determine the stable conformations of a series of alkylbenzenes. This study demonstrates, for the first time, the sensitivity of molecular jet spectroscopy in determining both the number of stable conformations as well as the geometry of various ethyl, propyl, and butyl substituents relative to the aromatic ring. Different rotamers with low barriers to interconversion, <5 kcal/mol, can be isolated in the supersonic jet expansion. Each observed conformation exhibits its own spectroscopic origin ($S_1 \rightarrow S_0$ transition) in a two-color time-of-flight mass spectrum (TOFMS). The number of stable conformations is then used to determine the minimum energy geometries of the substituent group. Previous identification of individual molecular conformations for such low barriers to interconversion has not been attainable with conventional techniques such as variable-temperature NMR.

Molecular conformation and its relationship to the chemical and physical properties of organic molecules have proven to be worthy of the intense effort expended since the pioneering work of D. H. R. Barton in the early 1950's.¹⁻⁴ Nonetheless, the experimental determination of the conformational preferences of many fundamentally important substituents is still lacking.⁵ This void is particularly prominent for substituents which have free energy barriers to conformational interconversion of less than ca. 5 kcal mol⁻¹ (1750 cm⁻¹), outside the range of variable-temperature NMR spectroscopy. In cases for which the individual conformations have not been "frozen out" and identified using the NMR technique, theoretical calculations have been of considerable value in facilitating conformational analysis and geometry assignments.⁴

Recently, we communicated the results of our initial studies using supersonic molecular jet laser spectroscopy as a novel tool for conformational analysis.⁶⁻⁸ This technique has allowed us to assign unequivocally the minimum energy geometries of aromatic ethyl and propyl substituents,⁹ and to determine the experimental values for torsional potential barriers in S_0 and S_1 for aromatic methyl groups.⁶ The jet spectroscopic technique allows the probing of both ground-state and electronically excited-state features of jet-cooled molecules.

The expansion process results in gas-phase molecules at near absolute zero temperature.⁹ Hence, ground-state energy minima can be isolated and studied, even when very low barriers to interconversion are present. Each stable conformation corresponding to a potential energy minimum generates, at least in principle, its own spectroscopic 0_0^0 transition, and conversely, each 0_0^0 transition is associated with a specific stable ground-state conformation. By examining the spectra of specifically substituted alkylbenzenes, one can "count" the number of stable ground-state conformations. Molecular geometry and conformation can be assigned from a knowledge of the number of ground-state energy minima a molecule possesses.

Alkylbenzenes can be divided into three categories with regard to substitution patterns: the aromatic ring can be bonded to a primary, secondary, or tertiary alkyl carbon atom (cf. Table I for the substituents examined herein). In this work, we are primarily interested in two conformational features: first, the orientation of the aromatic ring relative to the alkyl side chain, described by the torsion angle τ_1 (cf. Figure 1) (this is equivalent to defining the position of C_β relative to the plane of the benzene ring); and, second, the orientation of C_γ relative to C_{ring} (this is described by the torsion angle τ_2). Examination of molecular models and simple symmetry arguments indicate three conformational types for τ_1 , as indicated in Figure 1: planar, for which a $C_\alpha-C_\beta$ bond is in the plane of the aromatic ring, perpendicular, for which a $C_\alpha-C_\beta$ bond is perpendicular to the plane of the aromatic ring; and gauche, for which $0^\circ < \tau_1(C_{\text{ortho}}-C_{\text{ring}}-C_\alpha-C_\beta) < 90^\circ$.

In this report, the two-color time-of-flight mass spectra (TOFMS)¹⁰ and dispersed emission (DE) spectra of several alkyl-substituted benzenes (cf. Table I) are presented and analyzed in terms of the individual ground-state conformations of these nonrigid molecules.^{9,10} In particular, we consider the following

FNT 2

FNT 3

FNT 4

FNT 5-8

FNT 9

TBL I (003,32-33)

FIG 1 (006,35-36)

FNT 10-12

TXT03
PAR15

SEN09 8 issues. (a) Will supersonic molecular jet spectroscopy allow the
10 observation of different conformations of more complex alkyl-
SEN12 11 benzenes within the propyl and butyl series? (b) Do complex alkyl
12 substituents of the type ArCH_2R ($\text{R} = \text{alkyl}$) have $\tau_1 = 90^\circ$
SEN15 13 (perpendicular conformation, Figure 1)? (c) Can minimum energy
SEN18 14 conformations of ArCHR^1R^2 and $\text{ArCR}^1\text{R}^2\text{R}^3$ be observed? (d)
15 In addition to observing different conformations, will this technique
16 provide an experimental determination of their geometries?

TXT06

SEN03 PAR18 Results and Discussion

SEN03 1 A. Results of Previous Jet Studies. The barrier to internal
SEN09 2 rotation of the methyl group in toluene is extremely small due,
SEN12 3 in part, to the barrier's sixfold symmetry. Hence, assignment of
4 a stable conformational form for this molecule is not meaning-
SEN15 5 ful.^{6,13,14} Our observation of two 0% transitions in the TOFMS
16 for both 1,3-diethylbenzene and 1,4-diethylbenzene (corresponding
17 to the syn and anti conformations) and a single 0% transition for
18 ethylbenzene establishes that the perpendicular conformation 1a

AGID JA2B16a (015,35-36) KA

16 of the aromatic ethyl group in these compounds is present in the
48 global energy minimum.⁸

PAR21

SEN03 1 For propylbenzene, supersonic molecular jet spectroscopy has
2 shown that the propyl moiety exists in two stable, observable
3 conformations with respect to the aromatic ring: an anti 2 and

AGID JA2B16b (003,29-30) KA

SEN06 31 a gauche 3 conformation.⁷ Importantly, these results are consistent
32 only with a perpendicular orientation of the first torsion for both
33 of these conformations, i.e., $\tau_1(\text{C}_{\text{ortho}}-\text{C}_{\text{prop}}-\text{C}_\alpha-\text{C}_\beta) = 90^\circ$ as il-
SEN09 34 lustrated by 1b for both 2 and 3. [Beneath the structures 2 and
35 3 are the relative values of the MOMM-calculated¹⁴ steric energies
SEN12 36 (SE) for these rotamers. The SE values are indicative of the relative
37 stabilities of these conformations. Relative SEs are shown below
38 the structures for some of the other conformations discussed in
39 this paper.]

PAR24

SEN03 1 B. Compounds Containing an Aryl to a Primary Alkyl Bond
SEN09 2 (ArCH_2R). To probe the extent of the applicability of this su-
3 perersonic jet technique for the structure determination of more
4 complex molecules, we first studied a series of compounds con-
5 taining the $\text{Ar}-\text{CH}_2\text{R}$ substructure. 1-Ethyl-4-propylbenzene (4)

AGID JA2B16c (012, 3-4) KA

4 is an interesting combination of a molecule containing both the
SEN15 14 ethyl and propyl substituent. Extrapolating from the results
15 obtained for the ethylbenzenes and propylbenzenes cited above,
16 1-ethyl-4-propylbenzene would have, in principle, four origins: a
17 syn-anti 5a, a syn-gauche 5b, and the corresponding anti-anti
18 6a and anti-gauche 6b (the first descriptor specifying the relative
19 disposition of the two substituents with respect to each other, the
20 second descriptor specifying the conformation of the propyl
SEN18 21 substituent relative to the aromatic ring). As shown in Figure
22 2, four origin transitions are observed in the TOFMS of 4, one
23 each for the four energy minima (at 37 369.1, 37 372.7 and
SEN21 24 37 496.7, 37 497.3 cm^{-1}). Given the above structural logic and
25 the TOFMS of the ethyl- and propylbenzenes, the third doublet
26 at ca. 37 548 cm^{-1} then must be assigned as a torsional motion
27 of the propyl substituent group in accord with previous work.²⁻⁴

PAR27

SEN03 1 The TOFMS for the 0_0^0 region of the $S_1 \leftarrow S_0$ transition in
SEN06 2 isobutylbenzene (7) is presented in Figure 3. The spectrum

AGID JA2B16d (003,21-22) KA

SEN09 4 displays a single intense origin at 37 517.8 cm^{-1} . Two weak
4 features, assigned as isobutyl torsions, occur at 37 551.4 and
SEN12 13 37 559.6 cm^{-1} . Comparison of this spectrum to that of propyl-
14 benzene¹² is of value since the TOFMS of propylbenzene clearly
15 displays two origins, corresponding to conformations 2 (anti) and
SEN15 26 3 (gauche). Addition of a methyl group to the β position of the
SEN18 27 propyl chain results in an isobutyl group. The two possible
28 conformations for isobutylbenzene, analogous to 2 and 3, are 8a
29 and 9a.

PAR30

SEN03 1 Which of the two conformations 8a or 9a corresponds to the
13 minimum energy conformation of isobutylbenzene can be de-

FNT 13,14

FIG 2 (018, 6-7)

FIG 3 (003,16-17)

UNIT NO. 320
 Gal 3 JA2B16M JA881045M N111 1004 881216

TXT06
 PAR30

20 terminated experimentally from examination of the TOFMS of
 21 1-isobutyl-3-methylbenzene (10). Because of the asymmetrically
 22 substituted aromatic ring, the TOFMS for 10 would contain two
 23 origins if 8d and 8e were the minimum energy conformations.
 24 conformation 9d (=9e) would show only a single origin. The
 25 spectrum displayed in Figure 4 evidences two origins, at 36965.1
 26 and 37023.0 cm^{-1} (with 1e = 1e ring methyl torsions occurring
 27 $\sim 3 \text{ cm}^{-1}$ to lower energy of each origin¹⁰) so that 8d and 8e must
 28 be the minimum energy conformers. This conclusion is supported
 29 by our MOMM calculations, in which 8a is found to be more
 30 stable than 9a by ca. 0.7 kcal/mol as judged by steric energies.
 31 Statistical weights also favor 8a over 9a. These results reflect
 32 the greater stability of anti conformations relative to gauche
 33 conformations in isobutylbenzenes, a relationship also observed
 34 and calculated for the cases of propylbenzene and related mole-
 35 cules. Just as in the cases of propylbenzene and 3-methyl-1-
 36 propylbenzene, the number of conformations observed for iso-
 37 butylbenzene and 3-methylisobutylbenzene also dictate that τ_1 -
 38 ($\text{C}_{\text{ortho}}-\text{C}_{\text{para}}-\text{C}_a-\text{C}_\beta$) = 90° for the isobutyl substituent.¹⁰⁻¹²

FIG 4 (009, 7-8)

PAR33

39 The TOFMS of 1-isobutyl-2-methylbenzene (11) (Figure 5)
 40 contains two origins at 37036.0 and 37177.5 cm^{-1} . These pre-
 41 sumably correspond to 8b and 8c. A conformation 9 is not a
 42 significantly populated energy minimum for either isobutylbenzene
 43 or 1-isobutyl-3-methylbenzene, the observation of two origins for
 44 1-isobutyl-2-methylbenzene is further support for conformations
 45 8b and 8c for these isobutylbenzenes.

ENT 15

FIG 5 (003, 8-9)

PAR36

46 The TOFMS of neopentylbenzene (12) is shown in Figure 6.

FIG 6 (003, 6-7)

AGID JA2B16e (003,11-12)

KA

47 A single origin is observed at 37533.6 cm^{-1} . The observation of
 48 a single origin is consistent with the findings for propylbenzene
 49 and the isobutylbenzenes discussed above. As in the case for other
 50 compounds containing an aryl to a primary alkyl bond, τ_1 -
 51 ($\text{C}_{\text{ortho}}-\text{C}_{\text{para}}-\text{C}_a-\text{C}_\beta$) = 90° for neopentylbenzene.¹³ As illustrated
 52 in 12a, only a single staggered conformation is possible about τ_1 .
 53 These results are confirmed by MOMM calculations which indi-
 54 cate that the minimum energy conformation of 12 has a stag-
 55 gered arrangement about the C_1-C_2 bond (τ_1) and has τ_2 -
 56 ($\text{C}_{\text{ortho}}-\text{C}_{\text{para}}-\text{C}_a-\text{C}_\beta$) = ca. 90° .

PAR39

57 The TOFMS for the O_0^0 region of the $S_1 \rightarrow S_0$ transition of
 58 butylbenzene (13) is presented in Figure 7. The spectrum contains

FIG 7 (003,16-17)

AGID JA2B16f (003,21-22)

KA

59 one intense origin, at 37581.8 cm^{-1} with what appears to be a
 60 weaker origin to lower energy, at 37578.0 cm^{-1} . This latter peak
 61 is unlikely to be due to a methyl rotor transition for a methyl group
 62 so far removed from the chromophore.¹⁴ A variety of confor-
 63 mations, built on the anti and gauche conformations of propyl-
 64 benzene, can be imagined for butylbenzene. If the intense origin
 65 feature at 37581.8 cm^{-1} is indeed due to a single molecular
 66 conformation, it is most likely associated with the extended
 67 conformation 14aa (Table II), involving the staggered, all-anti
 68 form of the butyl group. This conformer involves the least amount
 69 of steric interference, according to our MOMM calculations.^{8,14}
 70 The assignment is consistent with our previous observations that
 71 the anti conformer is energetically favored over the gauche. The
 72 less intense origin at 37578.0 cm^{-1} is only 3.8 cm^{-1} lower in energy
 73 than the origin for 14aa. In propylbenzene, the gauche and anti
 74 conformer origins are separated by 49.2 cm^{-1} .¹⁵ This range of
 75 separation would also be expected between origins belonging to
 76 conformations of butylbenzene based on the gauche and anti
 77 conformations of propylbenzene. The observed separation of 3.8
 78 cm^{-1} in Figure 6 implies that the second origin (at 37578.0 cm^{-1})
 79 is probably due to a conformation such as 14ag. The terminal
 80 methyl group of the butyl chain is far enough from the π -system
 81 of the ring so that the effect of its orientation on the energy of
 82 the $\pi \rightarrow \pi^*$ transition should be relatively small, which is an ex-
 83 pectation consistent with the observed spacing of 3.8 cm^{-1} .

TBL II (015,29-30)

PAR42

84 We cannot at present account for the failure to observe ad-
 85 ditional O_0^0 transitions corresponding to the two other conformations
 86 of butylbenzene (gauche/gauche 14gg and gauche/anti 14ga)
 87 expected based on simple conformational analysis concepts or on
 88 our MOMM calculations (Table II). Conformational preferences
 89 for various alkylbenzenes, including butylbenzene, have recently
 90 been examined using CAMSEQ, MM2, and molecular dynamics

UNIT NO. 321
 Gal. 4 JA2B16M JA881045M V111 1004

06
 142

methods, with particular attention being placed on "trapped" conformations.⁴⁶ The theoretical approaches do not always lead to the same stability ordering of the various possible conformations,⁴⁶ and more detailed experimental studies are indicated.

R45

03

Previous papers from our laboratory have addressed the possibility that local, but not global, stable molecular conformations in nonrigid molecules or in van der Waals clusters can be depopulated through collisions in the molecular jet expansion.⁴⁷ In molecules or clusters for which shallow wells and small barriers to conformational changes exist, energetic collisions may depopulate local minima in the potential surface in favor of the deeper, global ones. Thus, in certain "sterically hindered" compounds (e.g., 2-propyltoluene,⁴⁸ 1,2-diethylbenzene,⁴⁹ and 1,2-dimethoxybenzene⁵⁰), not all of the conceivable locally stable orientations of the nonrigid moiety are equally populated. This unequal distribution of conformers in the final expansion equilibrium results in either unequal conformer spectroscopic intensities, or in extreme cases, the failure to observe specific 0₀⁺ transitions. Further evidence to substantiate the existence of this "kinetic effect" is presented below.

AR48

03

1-Butyl-3-methylbenzene (15) was examined with the hope that asymmetric substitution would confirm the anti-anti conformational assignment of the parent butylbenzene spectrum. Unfortunately, no ion signals could be observed. We attribute this finding to enhanced modes of nonradiative decay from S₁ of 15, thereby rendering the TOFMS experiment unfeasible in this case.

AR51

03

C. Compounds Containing an Aryl to a Secondary Alkyl Bond (ArCHR'R'). Isopropylbenzene (16) is the prototype of molecules

AGID JA2B16g (009, 3-4)

containing an aryl-secondary alkyl bond. Because the internal rotation barrier about the C₆H₅-C₁H₂ bond of isopropylbenzene is less than 5 kcal/mol,⁵¹ NMR studies have been unable to isolate and identify specific isopropyl conformations for sterically unhindered molecules.⁵²

PAR54

SEN03

SEN06

SEN09

SEN12

SEN15

SEN18

SEN21

SEN24

SEN27

SEN30

SEN33

SEN36

SEN39

SEN42

SEN45

SEN48

SEN51

SEN54

SEN57

SEN60

SEN63

SEN66

SEN69

SEN72

SEN75

SEN78

SEN81

SEN84

SEN87

SEN90

SEN93

SEN96

SEN99

SEN102

SEN105

SEN108

SEN111

SEN114

SEN117

SEN120

SEN123

SEN126

SEN129

SEN132

SEN135

SEN138

SEN141

SEN144

SEN147

SEN150

SEN153

SEN156

SEN159

SEN162

SEN165

SEN168

SEN171

SEN174

SEN177

SEN180

SEN183

SEN186

SEN189

SEN192

SEN195

SEN198

SEN201

SEN204

SEN207

SEN210

SEN213

SEN216

SEN219

SEN222

SEN225

SEN228

SEN231

SEN234

SEN237

SEN240

SEN243

SEN246

SEN249

SEN252

SEN255

SEN258

SEN261

SEN264

SEN267

SEN270

SEN273

SEN276

SEN279

SEN282

SEN285

SEN288

SEN291

SEN294

SEN297

SEN300

SEN303

SEN306

SEN309

SEN312

SEN315

SEN318

SEN321

SEN324

SEN327

SEN330

SEN333

SEN336

SEN339

SEN342

SEN345

SEN348

SEN351

SEN354

SEN357

SEN360

SEN363

SEN366

SEN369

SEN372

SEN375

SEN378

SEN381

SEN384

SEN387

SEN390

SEN393

SEN396

SEN399

SEN402

SEN405

SEN408

SEN411

SEN414

SEN417

SEN420

SEN423

SEN426

SEN429

SEN432

SEN435

SEN438

SEN441

SEN444

SEN447

SEN450

SEN453

SEN456

SEN459

SEN462

SEN465

SEN468

SEN471

SEN474

SEN477

SEN480

SEN483

SEN486

SEN489

SEN492

SEN495

SEN498

SEN501

SEN504

SEN507

SEN510

SEN513

SEN516

SEN519

SEN522

SEN525

SEN528

SEN531

SEN534

SEN537

SEN540

SEN543

SEN546

SEN549

SEN552

SEN555

SEN558

SEN561

SEN564

SEN567

SEN570

SEN573

SEN576

SEN579

SEN582

SEN585

SEN588

SEN591

SEN594

SEN597

SEN600

SEN603

SEN606

SEN609

SEN612

SEN615

SEN618

SEN621

SEN624

SEN627

SEN630

SEN633

SEN636

SEN639

SEN642

SEN645

SEN648

SEN651

SEN654

SEN657

SEN660

SEN663

SEN666

SEN669

SEN672

SEN675

SEN678

SEN681

SEN684

SEN687

SEN690

SEN693

SEN696

SEN699

SEN702

SEN705

SEN708

SEN711

SEN714

SEN717

SEN720

SEN723

SEN726

SEN729

SEN732

SEN735

SEN738

SEN741

SEN744

SEN747

SEN750

SEN753

SEN756

SEN759

SEN762

SEN765

SEN768

SEN771

SEN774

SEN777

SEN780

SEN783

SEN786

SEN789

TEXT06
PAR60

SEN18 7 presented in Figure 10. The spectrum displays only two intense
origins at 37226.6 and 37264.8 cm^{-1} , and thus 17 must be the
minimum energy conformation of the isopropyl group with respect
to the ring. Substitution of the ethyl group in the meta position
then yields conformers 22 and 23. This conclusion agrees with

AGID JA2B16h (021.16-17)

KA

our MOMM calculations and with the other literature data^{36,4}
which likewise predict 17 to be the stable conformation for iso-
propylbenzene.

PAR63
SEN03

We next examine the series of three compounds 24-26 which

AGID JA2B16i (003.10-11)

KA

is interesting because it embodies the partial substructures of both
the isopropyl and propyl substituents

PAR66
SEN03

The TOFMS of *sec*-butylbenzene (24) in the 0_0^0 region of the
 $S_1 \leftarrow S_0$ transition is presented in Figure 11 and contains a single
origin at 37627.1 cm^{-1} . The weaker feature occurring at 37661.3 cm^{-1}
is presumably due to torsional motion of the alkyl group as
discussed earlier. Only a single conformation for *sec*-butylbenzene
is observed. As a first approximation, $\tau(C_{\text{ortho}}C_{\text{meta}}C_{\text{para}}-C_{\text{ring}}-H_{\text{ortho}})$
should equal 0° for *sec*-butylbenzene (24) as found for iso-
propylbenzene.³⁹ The Newman projections of the three staggered
conformations are illustrated by 27-29. The most stable con-

AGID JA2B16j (015.13-14)

KA

formation of *sec*-butylbenzene is 29 by MOMM calculations,
nearly 1 kcal mol^{-1} more stable than 27 and 3 kcal mol^{-1} more
stable than 28. We therefore suggest that the minimum energy
conformation of *sec*-butylbenzene observed in the jet corresponds
to 29.

PAR69
SEN03

The TOFMS of 1-*sec*-butyl-2-methylbenzene (30) contains only

AGID JA2B16k (003.6-7)

KA

a single origin (Figure 12). MOMM calculations support the
observation of only a single conformation and that the preferred
conformation is 31.

PAR72
SEN03

(1,2-Dimethylpropyl)benzene (25) can, in principle, exist in
one or more of three staggered conformations 32-34. MOMM

AGID JA2B16l (003.16-17)

KA

calculations indicate that conformation 32, possessing only two
gauche-gauche interactions, is the ground-state energy minimum.
The TOFMS of 25 indicates two origins at 37556.6 cm^{-1} and
 37585.9 cm^{-1} . The origin to the red (low energy) is approximately
 10% the intensity of the second origin. We tentatively assign the
 37556.6 cm^{-1} origin as 33 and the 37585.9 cm^{-1} origin as 32 based
on the relative intensities of the two origins and the calculated
relative stabilities.

PAR75
SEN03

(1,2,2-Trimethylpropyl)benzene (26) has only one staggered
conformation, namely, 35, and its TOFMS shows a single origin

AGID JA2B16m (003.10-11)

KA

at 37585.8 cm^{-1} .

PAR78
SEN03

D. Compounds Containing an Aryl to a Tertiary Alkyl Bond
(ArCR¹R²R³). The one-color TOFMS of the 0_0^0 region of the S_1
 $\leftarrow S_0$ transition for jet cooled *tert*-butylbenzene (36) is presented

AGID JA2B16n (009.19-20)

KA

in Figure 13. The spectrum displays a single intense origin at
 37696.2 cm^{-1} , which means that only one of the three postulated
conformations (planar 37, perpendicular 38, gauche 39; cf. Table
IV) is an energy minimum, and therefore only one of these species
is present in the molecular jet. This is an important conclusion
because it implies that the only way that one origin can appear
in the TOFMS of 1-*tert*-butyl-4-ethylbenzene (40) as if the
minimum energy conformation of the *tert*-butyl group corresponds
to the planar conformation giving rise to conformation 41

PAR81

FIG 10 (015.10-11)

FIG 11 (003.21-22)

FIG 12 (003.13-14)

FIG 13 (009.24-25)

TBL IV (012.30-31)

XT06
AR81

EN03 1 The TOFMS for 40, presented in Figure 14, in fact, contains
EN06 13 only one origin at 37142.0 cm^{-1} . We therefore conclude that the
EN09 12 stable conformation for 1-*tert*-butyl-4-ethylbenzene must corre-
EN10 10 spond to 41. This in turn confirms that the minimum energy
EN16 18 conformation of the *tert*-butyl group in *tert*-butylbenzenes must
EN27 27 be the planar form and reconfirms the perpendicular conformation
EN35 35 of the aromatic ethyl substituent; these structural conclusions
EN46 46 follow if and only if the conformational assignments for both the
EN52 52 *tert*-butyl and ethyl substituents are correct. These conclusions
EN58 58 are further supported by our MOMM calculations which predict
EN64 64 the planar conformation to be the minimum energy conformation
EN70 70 of the *tert*-butyl group in 36 and 40. Given that both the cal-
EN76 76 culations and the experimental values are in agreement as to the
EN82 82 number and position of potential minima on those two surfaces,
EN88 88 we conclude that these determinations are valid.

PAR84

EN03 1 According to the above results, 1-*tert*-butyl-3-methylbenzene
EN06 16 (42) should exhibit a TOFMS containing two origins, corre-
EN12 12 sponding to conformations 43 and 44. The TOFMS for the 0_g

AGID JA2B16o (003.21-22)

LA

EN09 1 region of the $S_1 \leftarrow S_0$ transition for 42 using 140 psig of helium
EN12 12 is presented in Figure 15a. The most intense feature of the
EN18 18 spectrum occurs as a barely resolved doublet (due to the methyl
EN24 24 rotor transitions²⁻⁴) centered at 37136 cm^{-1} . Figure 15a also
EN30 30 displays two other intense features at 37165.0 and 37169.8 cm^{-1} .
EN36 36 Some of the weaker features that appear in the TOFMS of 42
EN42 42 correspond to additional internal rotational transitions of the ring
EN48 48 methyl rotor. The spectrum presented in Figure 15a is more
EN54 54 complicated than anticipated because there are three relatively
EN60 60 intense peaks.

PAR87

EN03 1 Because the three main features in the TOFMS of 42 are quite
EN06 16 intense, the exact assignment of origins and thus the number of
EN12 12 conformations for this molecule is not readily apparent. In order
EN18 18 to resolve this conformational analysis question, three additional
EN24 24 approaches were pursued: temperature-dependent spectra, to
EN30 30 investigate the possibility of hot bands (Figure 15); dispersed
EN36 36 emission studies (Figure 16); and methyl rotor calculations. The
EN42 42 latter demonstrate that the three features cannot be assigned to
EN48 48 a single conformation with (even intense) methyl rotor transitions.
EN54 54 On a first level of interpretation, Figures 15 and 16 suggest
EN60 60 somewhat contradictory conclusions about these data. The peak
EN66 66 at 37169.8 cm^{-1} in Figure 15 appears to be a hot band as its
EN72 72 intensity decreases with high-pressure argon expansion. Con-
EN78 78 clusively, the DE spectrum associated with the 37169.8 cm^{-1}
EN84 84 feature, a portion of which is depicted in Figure 16, indicates that
EN90 90 this feature is not a hot band because there are no transitions to
EN96 96 higher energy of the excitation energy.

PAR90

EN03 1 These three results (TOFMS, DE, and rigid rotor calculations)
EN06 16 can be rationalized by assigning the feature in question as due
EN12 12 to a second conformation of 42 which can be depopulated in the
EN18 18 argon expansion. The conformational energy balance (well depth,
EN24 24 barrier heights, and surface shape) in this instance must be such
EN30 30 that the more energetic collisions with argon rather than with
EN36 36 helium emphasize the "kinetic effect" described below. MOMM
EN42 42 calculations predict that 43 and 44 do indeed correspond to energy
EN48 48 minima, being nearly identical in terms of steric energy. The
EN54 54 barrier between the two minima (calculated to be 0.5 kcal mol^{-1})
EN60 60 should be of low enough energy that argon collisions can convert
EN66 66 all of the molecules to a single conformation. As shown in Table
EN72 72 IV, the planar conformation 37 of the *tert*-butyl substituent is
EN78 78 further confirmed.

PAR93

EN03 1 1,3-Di-*tert*-butylbenzene (45) represents the most highly sub-
EN06 16 stituted and largest molecule in terms of molecular weight ex-
EN12 12 amined in these studies. The TOFMS for the 0_g region of the
EN18 18 $S_1 \leftarrow S_0$ transition for 45 using 140 psig of helium is presented
EN24 24 in Figure 17. We attribute the three features at 37335.6 , 37388.1 ,
EN30 30 and 37410.2 cm^{-1} to conformations 46-48, although at this stage

AGID JA2B16p (009.15-16)

LA

EN12 20 we cannot assign conformations to particular transitions. MOMM
EN18 18 calculations indicate that 46-48 are of nearly equal stability, and
EN24 24 hence the unequal intensity of the three transitions may again be
EN30 30 due to some kinetic phenomena during the expansion process.
EN36 36 Chart IV summarizes the results obtained for *tert*-butyl aromatics.

FIG 14 (003.9-10)

FIG 15 (006.25-26)

FIG 16 (006.31-32)

FIG 17 (006.25-26)

TXT06
 PAR96

SEN03 E. Kinetic Factors in the Expansion Process. Previous papers
 SEN04 from our laboratory have addressed the possibility that locally
 1 but not globally stable molecular conformations in nonrigid
 2 molecules or in van der Waals clusters can be depopulated through
 3 collisions in the molecular jet expansion.^{1,2} In molecules or clusters
 4 for which shallow wells and small barriers to conformational
 5 changes exist, energetic collisions may, in principle, depopulate
 6 local minima in the potential surface in favor of the deeper global
 7 ones. The intensity ratios for the 0₀ transitions of the various
 8 conformers reflect the populations of these conformers which exist
 9 at the terminal beam temperature ($T_{\text{term}} < 1$ K, $T_{\text{jet}} = 2-5$ K,
 10 and $T_{\text{in}} = 10-20$ K). These populations are not equilibrium
 11 populations representative of any particular temperature, however,
 12 as they are also affected by the potential surface shape and the
 13 kinetic pathway(s) to this terminal temperature.

PAR99

SEN03 Relative intensities of origins are thus rather unpredictable based
 SEN04 on structural expectations or theoretical estimates. Numerous
 1 cases exist for which the intensities appear to follow intuition or
 2 theory (e.g., 1,3- and 1,4-diethylbenzene,³ 1-methoxy-3-propyl-
 3 benzene,⁴ 1-methoxy-3-methylbenzene,⁵ etc.). On the other hand,
 4 for 1,3-di-*tert*-butylbenzene reported herein (figure 1), expec-
 5 tations of three nearly equally intense 0₀ transitions are not met.
 6 For cases of "sterically hindered" compounds, e.g., 1-methyl-2-
 7 propylbenzene and 1,2-diethylbenzene, equal populations of the
 8 various possible conformations are not expected and the 0₀
 9 transition intensities are very different. Unequal distribution of
 10 conformers in the final expansion equilibrium results in unequal
 11 spectroscopic intensities for the different conformations.

PAR102

SEN03 To some extent, the expectation or prediction of a kinetic effect
 1 is based on ground-state equilibrium distributions calculated from
 2 calculated steric energies or heats of formation rather than from
 3 any independent experimental data. MOMM calculations allow
 4 us to determine the relative populations of the various conform-
 5 ations of a system. If the conformations have free energies within
 6 ca. 1 kcal mol⁻¹, they should be populated at room temperature,
 7 however, if the free energy difference is much larger than this,
 8 the higher energy forms should be effectively absent from the
 9 populated conformations. Thus the calculated energy predictions
 10 play a role in the number of conformations expected to be observed
 11 in our experiments. Hence the identification of a kinetic effect
 12 is somewhat tied to calculations of conformational free energies.^{4,6}
 13 Experimental evidence for a kinetic effect can sometimes be ob-
 14 tained, for example, by performing TOFMS experiments using
 15 different expansion gases.

PAR105

SEN03 Comparison of Conformational Analysis Capabilities by Jet and
 SEN04 Other Spectroscopic Techniques. We emphasize that one of the
 1 most fundamental consequences of this work is the spectroscopic
 2 observation of specific conformations of simple alkylbenzenes.
 3 Because of the low barriers to internal rotation of the substituents
 4 in these molecules, previous experimental studies have, with few
 5 exceptions, observed only averaged spectroscopic properties for
 6 the individual conformations present.

PAR108

SEN03 For example, the barrier to rotation about a nonhindered
 SEN04 aromatic *tert*-butyl group is quite low, ca. 0.5 kcal mol⁻¹. NMR
 1 is not presently capable of observing the individual conformations
 2 of such asymmetrically substituted *tert*-butyl systems as reported
 3 above. Yamamoto and Ōki¹⁰ reported the first "unambiguous"¹⁰
 4 observation of restricted rotation for an aromatic *tert*-butyl-C
 5 2 group in 1986 for the specially designed, highly hindered
 6 molecule 49. An energy barrier of 9.2 kcal mol⁻¹ for rotation

FNT 19

AGID JA2B16q 1009.28-291

about the C₁-*tert*-butyl group was found.¹

PAR111

SEN03 The most obvious difference between the Yamamoto and Ōki
 1 results¹⁰ and those reported herein is that laser jet spectroscopy
 2 is able to observe specific conformations of *unhindered* aromatic
 3 substituted *tert*-butyl groups. A more subtle distinction is that
 4 the NMR study observed individual spectroscopic signals for the
 5 methyl groups of a molecule which has only a *single tert*-butyl
 6 conformation.¹⁰ On the other hand, we have observed two or more
 7 stable conformations of a specific compound which differ from
 8 each other by the arrangement in space of the *tert*-butyl group
 9 itself. Thus, we are able to observe spectroscopic properties from
 10 the two stable conformations of 1-*tert*-butyl-3-methylbenzene and
 11 from the three stable conformations 1,3-di-*tert*-butylbenzene.

PAR114

TXT06
PAR114

SEN01 The motion of the isopropyl group and related secondary alkyl substituents (e.g., cyclopropyl, cyclohexyl, carbomethoxyl, etc.) has been sufficiently slowed down and detected by NMR spectroscopy, but only in systems for which two adjacent bulky groups significantly increase the barrier to rotation.¹²⁰ A low-resolution microwave study of meta-substituted isopropylbenzenes has resulted in the observation of two spectroscopically distinguishable band series, one each for the two minimum energy conformations.¹²¹ On the other hand, we have observed the stable conformations of the simple secondary alkyl-substituted aromatics, 1-methyl-3-isopropylbenzene (two conformations) and 1-ethyl-3-isopropylbenzene (two conformations). Again note the sterically unhindered environment of these substituents.

FNT 20

PAR117

SEN01 As found for the *tert*-butyl, isopropyl, and analogous substituents, compounds containing aryl to primary alkyl groups (ArCH₂R) have very low barriers to conformational interconversion unless found in sterically encumbered environments. We have previously reported the observation of two conformations for both 1,3- and 1,4-diethylbenzene (the anti and syn conformations),¹²² propylbenzene (anti and gauche conformations),¹²³ and 1-methyl-3-propylbenzene (one anti and two gauche conformations).¹²⁴ Low-resolution microwave studies were performed by True et al.¹²⁵ on several ethylbenzenes but could only have observed a single ground-state energy minimum; hence, the crucial experiment of studying molecules which possess two or more stable conformations was not reported. Four origin transitions are observed for 1-ethyl-4-propylbenzene, due to the syn and anti conformations (relative to the perpendicular ethyl substituent) of both the anti and gauche conformations of the propyl substituent. **5a-5b** and **6a-6b**.

PAR120

SEN01 Recently Sandstrom and co-workers reported one of the very few studies on systems Ar-CH₂R for which R is a bulky alkyl group (in these cases, R = isopropyl and *tert*-butyl, leading to isobutyl and neopentyl substituents).¹²⁶ Using dynamic NMR, they were able to observe the syn and anti conformations (**50** and **51**, respectively) of the 3-alkyl-3-isobutylrhodanines (R¹ = methyl

AGID JA2B16r (006.17-18)

HA

SEN09 and phenyl). This is equivalent to observing the conformations about τ_2 (cf. **52**). In these cases, however, they did not observe

AGID JA2B16s (009.12-13)

HA

SEN10 signals for the rotational conformations about the second torsion, τ_2 , e.g., **52**. In the current study, two conformations are noted for both 1-isobutyl-2-methylbenzene (**8b** and **8c**) and 1-isobutyl-3-methylbenzene (**8d** and **8e**). The individual conformations depicted by **8** represent torsional isomerism about τ_2 . Hence, the laser jet spectroscopy method can observe conformational isomers about both τ_1 and τ_2 .

TXT09

SEN01

PAR123

SEN01

Summary and Conclusions

This study demonstrates the use of supersonic molecular jet laser spectroscopy to establish the existence of various stable conformations of the following types of alkyl-substituted aromatic compounds: those containing aryl to primary alkyl bonds (ethyl, propyl, isobutyl, neopentyl), aryl to secondary alkyl bonds (isopropyl, *sec*-butyl), and aryl to tertiary alkyl bonds (*tert*-butyl). Attention is focused upon two conformational parameters: the position of C₂ and C₃ of ArC₁-C₂-C₃-R (R = H or alkyl) molecular types, i.e., τ_1 and τ_2 in Figure 1.

PAR126

SEN01

We have demonstrated the capability of laser jet spectroscopy by investigating substrates in which only small structural features distinguish one conformational energy minimum from another. The observation of two or more O₀ transitions indicates the capability of these high-resolution techniques to observe two (and presumably more) conformations having nearly identical free energy. The most demanding choice, from a structural point of view, would be compounds possessing two or more distant and noninteracting substituents. Numerous substrates meeting this criterion have been examined.

PAR129

SEN01

The ground-state conformational energy minima of various asymmetrically substituted dialkylbenzenes are experimentally established by matching the number of observed O₀ origin transitions to the various "geometrical" possibilities. Thus, the ArCH₂-C bond of aromatic to primary alkyl substituents, e.g.,

TXT09
PAR129

1 ethylbenzene π in Figure 1) is perpendicular to the plane of the
2 aromatic ring, and the C-H bond in aryl to secondary alkyl bonds
3 (e.g., in isopropylbenzene) is in the plane of the aromatic ring.
4 Similarly, jet spectroscopy has established that one of the methyl
5 groups in *tert*-butylbenzene (an example of an aryl to tertiary alkyl
6 bond containing substrate) is in the plane of the aromatic ring.

PAR132

1 The second torsion of the aromatic alkyl side chain τ_2 (cf. Figure
2) is also established for a number of compounds, including
3 propylbenzenes and butylbenzenes. In these cases, two ground-
4 state minima are observed for each compound. Unfortunately,
5 information regarding the third torsion τ_3 ($C_1-C_2-C_3-C_4$) is not
6 obtained in the only compound possessing a C_{10} , namely, butyl-
7 benzene. The structural variability at C_3 may be too far removed
8 from the aromatic chromophore in the molecule to allow structural
9 discrimination, even by these sensitive methods.

PAR135

1 This work strongly supports our previous conclusions that jet
2 spectroscopy is an excellent technique for the observation and
3 identification of conformations of aromatic molecules which in-
4 terconvert with very low energy barriers. The experimental ob-
5 servations are complemented by molecular orbital-molecular
6 mechanics (MOMM) calculations which estimate the stabilities
7 of various conformations of these molecules.

TXT12

Experimental Section

SEN03

PAR138

1 The time-of-flight mass spectrometer was as described elsewhere.³
2 The TOFMS experiment used a R. M. Jordan pulsed valve. Both helium
3 and argon were used as carrier gases, as specified for each experiment.
4 All TOFMS experiments were performed at room temperature, and
5 involved one-color two-photon photoionization.

PAR141

1 Dispersed emission (DE) experiments were carried out in a fluores-
2 cence excitation chamber described previously.⁴ Four optics were used to
3 collect and focus the emission onto the slit of an F8-2051 GCA
4 McPherson 1-m scanning monochromator with a dispersion of 2.78 Å/
5 mm in third order of a 1200 groove/mm, blazed grating. Expansion
6 of the gas into the chamber was achieved with a Quanta Ray PSV-2
7 pulsed valve with a 500- μ m pinhole located \sim 1 cm from the laser beam.
8 Samples were placed in the head of the valve and heated to 65–70 °C
9 to achieve a greater concentration in the jet. Helium at 70 psi was used
10 as the carrier gas except as otherwise noted. The alkylbenzenes¹² 12,
11 13, 15, 16, 20, 21, 24, 36, 40, 42, and 45 were purchased from either
12 Aldrich Chemical Co. or Wiley Organics. The purity of these materials
13 was determined by GC and NMR spectroscopy prior to their use. Ex-
14 perimental details for the preparation of 4, 10, 11, 15, 25, 26, and 30 are
15 given in the Supplementary Material.

PAR144

1 Empirical force field calculations are performed using the molecular
2 orbital-molecular mechanics (MOMM-XS) algorithm of Rao.^{14,15} This
3 force field has been specifically parametrized for aromatic ring systems
4 and is known to reproduce experimental geometries and energies.
5 MOMM has also been used to correlate steric energies with the rates of
6 certain aromatic ring additions¹⁶ and pyrolysis reactions.¹⁷ The
7 ground-state calculations are performed using complete geometry opti-
8 mization to determine the ground-state energy minimum (the stable
9 conformation) and to estimate the potential energy barriers to rotation
10 about the $C_{\text{aromatic}}-C_{\alpha}$ and $C_{\alpha}-C_{\beta}$ bonds, as well as about the torsions τ_1
11 ($C_{\text{aromatic}}-C_{\alpha}-C_{\beta}-C_{\gamma}$) and τ_2 ($C_{\text{aromatic}}-C_{\alpha}-C_{\beta}-C_{\gamma}$) respectively.

TXT15

PAR147

1 **Acknowledgment.** We thank J. Campbell for obtaining the
2 NMR spectra, D. Seal and T. Sinkiewicz for secretarial assistance,
3 R. Ferguson, A. Kassman, B. LuRov, and C. Lilly for their en-
4 couragement and enthusiasm regarding this work, and J. B. Paine
5 III for helpful discussions.

TXT18

PAR150

1 **Supplementary Material Available:** Experimental details for
2 the preparation of 4, 10, 11, 15, 25, 26, and 30 including spectro-
3 scopic data and elemental analyses for these compounds (5
4 pages). Ordering information is given on any current masthead
5 page.

FN002

FN003

1 (1) (a) Philip Morris Research Center; (b) Colorado State University; (c)
2 Current address: Baker Performance Chemicals, 3923 Essex Lane, Houston,
3 TX 77027.

FN003

FN006

1 (2) For reviews of this subject and leading references, see: (a) Barton, D.
2 H. R. Some Recollections of Gap Jumping. In *Profiles, Pathways, and*
3 *Dreams: The Development of Modern Organic Chemistry*; Seeman, J. I., Ed.;
4 American Chemical Society: Washington, D.C., in press; (b) Ramsev, O.
5 B. *Stereochemistry*; Heyden: London, 1981; (c) Eliel, E. L.; Allinger, N. L.;
6 Wilen, S. H. *Topics in Stereochemistry*; Wiley-Interscience: New York, Vol.
7 1, 1977; (d) Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. *Con-*
8 *formational Analysis*; Wiley-Interscience: New York, 1965; (e) Seeman, J.

ENT 21

ENT 22, ENT 23

- FNN03
FNP06
SEN01
FNN04
FNP09
SEN01
SEN06
SEN09
SEN12
FNN05
FNP12
SEN01
SEN06
SEN09
SEN12
SEN15
SEN18
FNN06
FNP15
SEN01
FNN07
FNP18
SEN01
FNN08
FNP21
SEN01
FNN09
FNP24
SEN01
FNN10
FNP27
SEN01
FNN11
FNP30
SEN01
SEN06
SEN09
SEN12
SEN15
SEN18
SEN21
SEN24
SEN27
SEN30
SEN33
FNN12
FNP33
SEN01
SEN06
SEN09
SEN12
SEN15
FNN13
FNP36
SEN01
FNN14
FNP39
SEN01
FNN15
FNP42
SEN01
FNN16
FNP45
SEN01
SEN06
SEN09
FNN17
FNP48
SEN01
SEN06
FNN18
FNP51
SEN01
SEN06
FNN19
FNP54
SEN01
SEN06
FNN20
FNP57
SEN01
SEN06
1. *Chem. Rev.* **1983**, *63*, 83.
- (3) Ōki, M. *Applications of Dynamic NMR Spectroscopy to Organic Chemistry*, VCH Publishers, Deerfield Beach, FL, 1985. (b) Jackman, L. M., Cotton, F. A. *Dynamic NMR Spectroscopy*, Wiley, New York, 1975. (c) Berg, U., Liljefors, T., Roussel, C., Sandström, J. *Adv. Chem. Res.* **1985**, *19*, 80. (d) Berg, U., Sandström, J. *Adv. Phys. Org. Chem.*, in press.
- (4) (a) Osawa, E., Musso, H. *Top. Stereochem.* **1982**, *13*, 117. (b) Burkert, U., Allinger, N. L. *Molecular Mechanics*, ACS Monograph 177, American Chemical Society, Washington, DC, 1982. (c) Clark, T. *Handbook of Computational Chemistry*, Wiley, New York, 1985. (d) Hehre, W. J., Radom, L., Schleyer, P. v. R., Pople, J. A. *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1986. (e) Pross, A., Radom, L. *Adv. Phys. Org. Chem.* **1981**, *13*, 1. (f) Grunewald, G. L., Creele, M. W., Weintraub, H. J. R. *J. Comput. Chem.* **1988**, *9*, 315.
- (5) Breen, P. J., Warren, J. A., Bernstein, E. R., Seeman, J. I. *J. Am. Chem. Soc.* **1987**, *109*, 3453.
- (6) Breen, P. J., Warren, J. A., Bernstein, E. R., Seeman, J. I. *J. Chem. Phys.* **1987**, *87*, 1917.
- (7) Breen, P. J., Warren, J. A., Bernstein, E. R., Seeman, J. I. *J. Chem. Phys.* **1987**, *87*, 1927.
- (8) Breen, P. J., Bernstein, E. R., Seeman, J. I. *J. Chem. Phys.* **1987**, *87*, 1269.
- (9) Bernstein, E. R., Law, K., Schauer, M. *J. Chem. Phys.* **1984**, *80*, 201.
- (10) (a) The name "one- (and two-) color time-of-flight mass spectroscopy" is generally employed to describe the following experiment: A sample is irradiated with a laser of energy ν_1 , resulting in the generation of the first excited singlet state ($S_0 \rightarrow S_1$). A second photon ν_2 subsequently ionizes those molecules in S_1 ($S_1 \rightarrow I^+$). The ions are detected in given mass channels by time-of-flight mass spectroscopy, such that only ion current representing a chosen m/z is recorded. The energy of the ν_2 laser is changed, and an absorption spectrum of a mass-selected species is obtained. (b) In pioneering work, Smalley and co-workers have reported ^{13}C fluorescence excitation (FE) spectra and dispersed fluorescence spectra of a set of alkylbenzenes. These studies did not examine in detail the conformational analysis of the compounds. In addition, because the FE results are not mass selected, there could be some ambiguity regarding the source of some of the transitions. Ito et al.¹⁶ have examined intramolecular electronic energy transfer of bichromophoric molecules [e.g., 1-(10-10-10)-3-(p-10-10)propane] using these techniques. Ito's Tohoku University group has also studied conformational problems in phenols and naphthols¹⁷ and anisoles.¹⁸ One of us (E. R. B.) has previously examined the TOFMS of propylbenzene clusters with methane, ethane, and propane.¹⁹
- (11) (a) Hopkins, J. B., Powers, D. E., Smalley, R. E. *J. Chem. Phys.* **1980**, *72*, 5039. (b) Hopkins, J. B., Powers, D. E., Mukamel, S., Smalley, R. E. *J. Chem. Phys.* **1980**, *72*, 5049. (c) Ebata, T., Suzuki, Y., Mikami, N., Miyashi, T., Ito, M. *Chem. Phys. Lett.* **1984**, *107*, 597. (d) Oikawa, A., Abe, H., Mikami, N., Ito, M. *J. Phys. Chem.* **1984**, *88*, 5180. (e) Yamamoto, S., Okuyama, K., Mikami, N., Ito, M. *Chem. Phys. Lett.* **1986**, *125*, 1.
- (12) Law, K. S., Bernstein, E. R. *J. Chem. Phys.* **1985**, *82*, 2856.
- (13) Kreiner, W. A., Rudolph, H. D., Tan, B. T. *J. Mol. Spectrosc.* **1973**, *48*, 96.
- (14) Kao, J. *J. Am. Chem. Soc.* **1987**, *109*, 1477.
- (15) (a) Pettersson, I., Rang, A., Sandström, J. *Acta Chem. Scand.* **1986**, *B40*, 751. (b) Roussel, C., Gaillo, R., Metzger, J., Sandström, J. *Org. Magn. Reson.* **1980**, *14*, 120. (c) Roussel, C., Blaise, B., Gaillo, R., Metzger, J., Sandström, J. *Org. Magn. Reson.* **1980**, *14*, 160.
- (16) (a) Seeman, J. I., Secor, H. V., Breen, P. J., Bernstein, E. R. *J. Chem. Soc. Chem. Commun.* **1988**, 191. (b) Breen, P. J., Bernstein, E. R., Secor, H. V., Seeman, J. I. *J. Am. Chem. Soc.*, in press.
- (17) The rotational barrier about the C_1-C_2 bond in propylbenzene has been reported to be 0.25 kcal/mol²⁰ by microwave investigations,²¹ and 2.0 kcal/mol²² by NMR studies.²³ Recent MQM calculations have estimated a barrier of 2.3 kcal/mol.²⁴
- (18) (a) True, N. S., Farag, M. S., Guhn, R. K., MacGregor, M. A., Radhakrishnan, J. *J. Phys. Chem.* **1983**, *87*, 4622. (b) Schaefer, T., Parr, W. J. E., Danchura, W. *J. Magn. Reson.* **1977**, *25*, 167.
- (19) (a) Yamamoto, G., Ōki, M. *Tetrahedron Lett.* **1986**, 49. (b) For an earlier NMR study, France et al.²⁵ observed ^1H resonances for the individual

FNN20
FNP57

methvl groups of some 1,8-di-*tert*-butyl-naphthalenes at low (<140 °C) temperature. In these cases, substantial deviation from normal sp²-hybridization obtains. (c) Anderson, J. E., Franck, R. W., Mandella, W. L. *J. Am. Chem. Soc.* 1972, 94, 4608. (d) Handel, J., White, J. G., Franck, R. W., Yuh, Y. H., Allinger, N. L. *J. Am. Chem. Soc.* 1977, 99, 3345.

FNN21
FNP60

(20) See also Nilsson, I., Berg, C., Sandström, J. *Acta Chem. Scand.* 1984, B38, 491.

FNN22
FNP63

(21) Kao, J., Leister, D., Sito, M. *Tetrahedron Lett.* 1985, 2403.

FNN23
FNP66

(22) Seeman, J. I. *Pure Appl. Chem.* 1987, 59, 1661.

FNN24
FNP69

(23) Houminer, Y., Kao, J., Seeman, J. I. *J. Chem. Soc., Chem. Commun.* 1984, 1608.

FNN24
FNP69

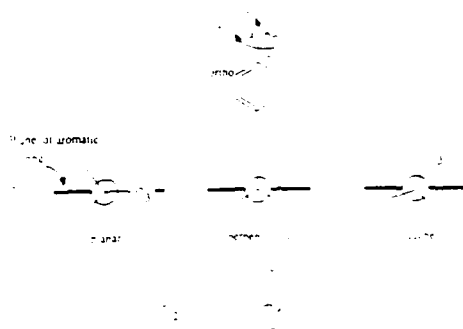


Figure 1. Definition of torsional angles which specify conformational geometries of the molecules examined in this study.

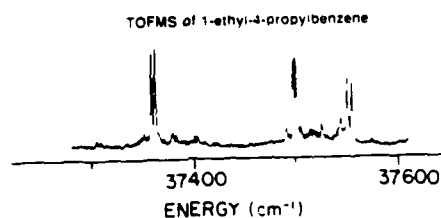


Figure 2. TOFMS of the 0% region of 1-ethyl-4-propylbenzene (4). The spectrum consists of four origins at 37569, 37572, 37496, and 37497 cm⁻¹ corresponding to four stable conformations for this molecule (see text).

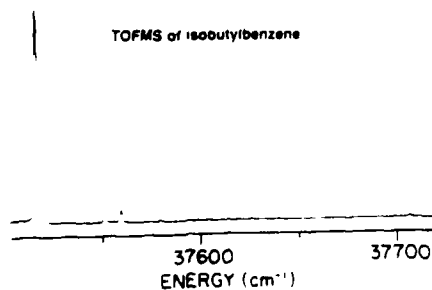


Figure 3. TOFMS of the 0% region of the S₀ → S₁ transition of isobutylbenzene (7). The spectrum displays a single origin at 37517.8 cm⁻¹. The weak features at 37551.4 and 37559.6 cm⁻¹ are attributed to torsional motion of the isobutyl group.

FNN24
FNP69

TOFMS of 1-isobutyl-3-methylbenzene

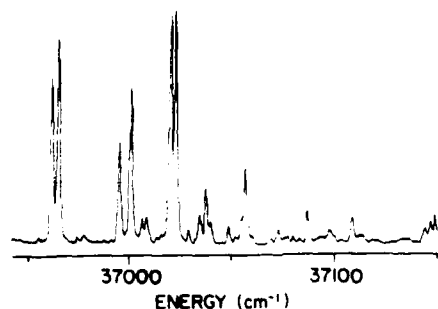


Figure 4. TOFMS of the 0_0^0 region of the $S_0 \rightarrow S_1$ transition of 1-isobutyl-3-methylbenzene (10). The spectrum contains two origins at 36965.1 and 37023.0 cm⁻¹. The peaks occurring 3 cm⁻¹ lower in energy than these origins are due to ring methyl torsions.

TOFMS of 1-isobutyl-2-methylbenzene

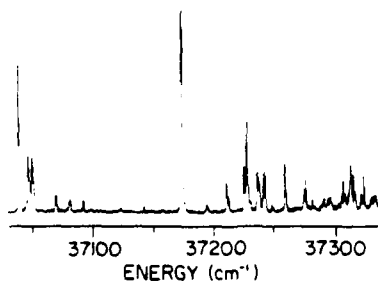


Figure 5. TOFMS of the 0_0^0 region of 1-isobutyl-2-methylbenzene (11). Two origins are observed in the spectrum at 37036.0 and 37171.8 cm⁻¹.

TOFMS of neopentylbenzene

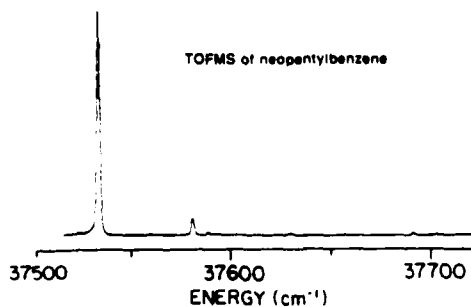


Figure 6. TOFMS of the 0_0^0 region of neopentylbenzene (12). The spectrum shows only one origin at 37533.6 cm⁻¹. Weaker features, higher in energy to the origin, are attributed to low-frequency torsional motions of the neopentyl group.

FNN24
FNP69

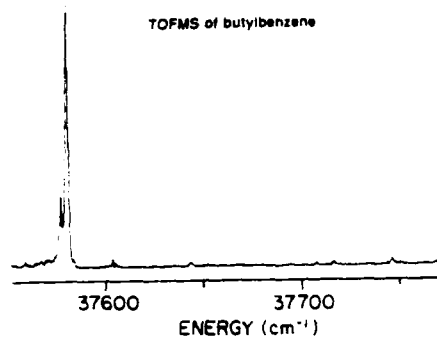


Figure 7. TOFMS of the 0_0^0 region of the $S_1 \leftarrow S_0$ transition of butylbenzene (13). The intense feature at 37578.0 cm^{-1} is assigned to the staggered, all-anti conformation of the butyl group (14aa). The weaker feature at 37578.0 cm^{-1} is also assigned as a separate origin, corresponding to 14ag.

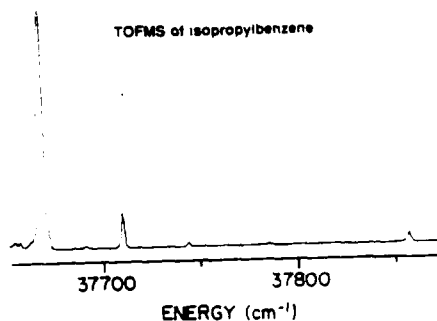


Figure 8. TOFMS of the 0_0^0 region for the $S_1 \leftarrow S_0$ transition of isopropylbenzene (16). The sole origin occurs at 37668.5 cm^{-1} . The weaker feature at 37710.0 cm^{-1} is attributed to torsional motion of the isopropyl group.

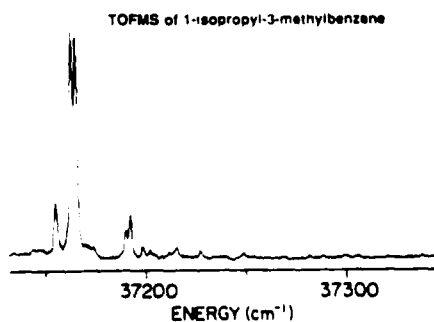


Figure 9. TOFMS of the 0_0^0 region of the $S_1 \leftarrow S_0$ transition of 1-isopropyl-3-methylbenzene (20). The peak at 37165.9 cm^{-1} is an origin which forms a doublet with the peak at 37164.0 cm^{-1} . This latter peak is attributed to the $1e \leftarrow 1e$ internal rotational transition of the ring methyl rotor. The weaker peak at 37156.0 cm^{-1} is also assigned as an origin. The presence of two origins eliminates 18 as a possible stable conformation.

FNN24
FNP69

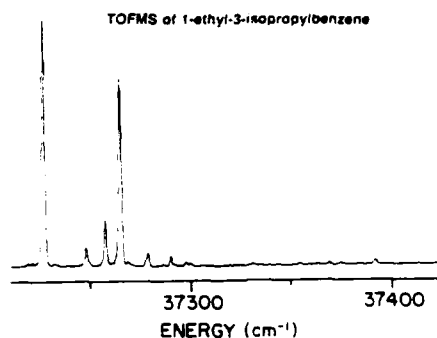


Figure 10. TOFMS of the 0_0^0 region of the $S_1 \rightarrow S_0$ transition of 1-ethyl-3-isopropylbenzene (21). The two origins of the spectrum, at 37226.6 and 37264.8 cm⁻¹, help identify the stable conformation of the isopropyl group as 17, as outlined in the text.

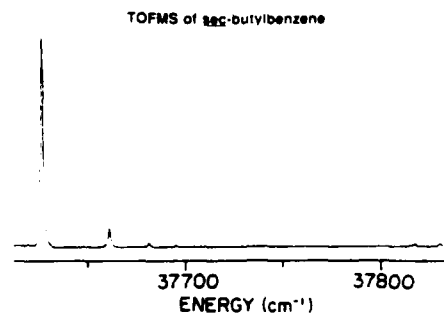


Figure 11. TOFMS of the 0_0^0 region of the $S_1 \rightarrow S_0$ transition of *sec*-butylbenzene (24). The spectrum displays a single origin at 37627.1 cm⁻¹. The weak feature at 37661.3 cm⁻¹ is attributed to torsional motion of the *sec*-butyl group.

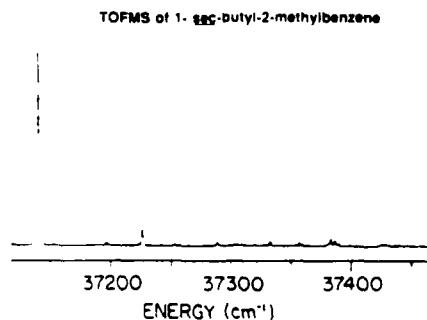


Figure 12. TOFMS of the 0_0^0 region of 1-*sec*-butyl-2-methylbenzene (30). The spectrum contains only a single origin. This is consistent with MOMM calculation which predicts only one stable conformation for this molecule (see text).

FNN24
FNP69

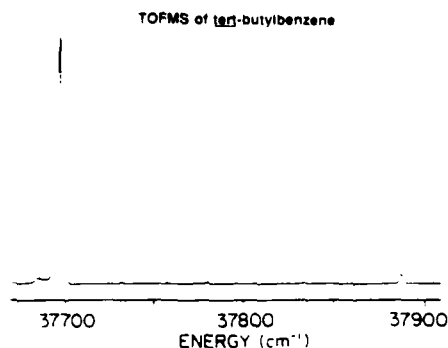


Figure 13. The one-color TOFMS of the 0_0^0 region of the $S_1 \leftarrow S_0$ transition of *tert*-butylbenzene (36). The single origin in the spectrum occurs at 37696.2 cm^{-1} and is indicative of a single stable molecular conformation.

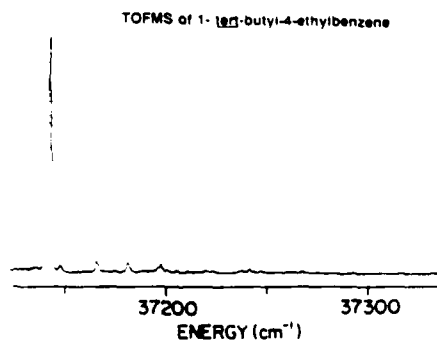


Figure 14. TOFMS of the 0_0^0 region of the $S_1 \leftarrow S_0$ transition of 1-*tert*-butyl-4-ethylbenzene (40). The fact that this spectrum contains only one origin at 37142 cm^{-1} identifies the stable molecular conformation of the *tert*-butyl group as 31.

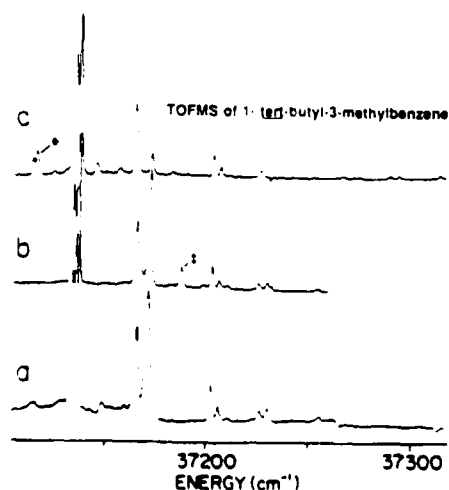


Figure 15. TOFMS of the 0_0^0 region of the $S_1 \leftarrow S_0$ transition of 1-*tert*-butyl-3-methylbenzene (42), using (a) 140 psig of helium; (b) 1% CF_4 in 100 psig of helium; and (c) 20 psig of argon as the carrier gas. The peaks indicated by the * and † are due to argon and CF_4 clusters, respectively, decomposing into the 1-*tert*-butyl-3-methylbenzene mass channel. The intense peaks at 37137.0 and 37169.8 cm^{-1} are origins for two different molecular conformations. The 37169.8 cm^{-1} peak disappears in (c) because of a kinetic effect discussed in the text.

FNN24
FNP69

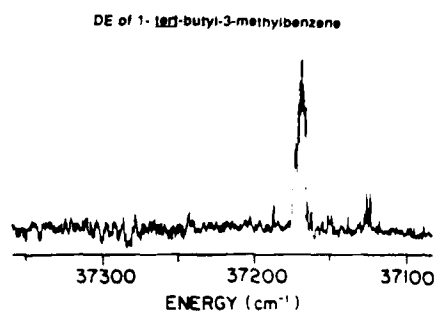


Figure 16. DE spectrum for 1-*tert*-butyl-3-methylbenzene (42) obtained by pumping the 37169.8-cm⁻¹ feature in Figure 15a. Resolution is 7.6 cm⁻¹. The absence of a feature to higher energy of the peak at 37169.8 cm⁻¹ helps to preclude the assignment of the 37169.8-cm⁻¹ feature in Figure 15, a and b, as a hot band.

TOFMS of 1,3-di-*tert*-butylbenzene

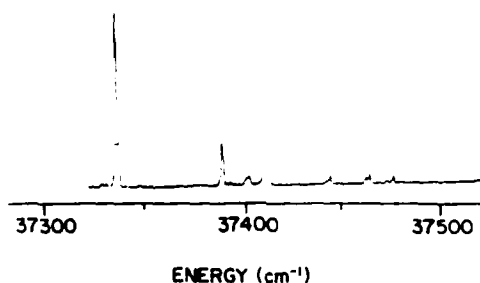


Figure 17. TOFMS of 1,3-di-*tert*-butylbenzene (45). The three most intense peaks in the spectrum at 37335.6, 37388.1, and 37410.2 cm⁻¹ are assigned to three different spectroscopy origins corresponding to three stable conformations for this molecule.

The number of words in this manuscript is 7392.

The manuscript type is A.

Running Heads

Conformations of Alkylbenzenes by TOFMS

Seeman et al.

Author Index Entries

Seeman, J. I.

Secor, H. V.

Breen, P. J.

Grassian, V. H.

Bernstein, E. R.

Supplementary Material Available

Text Page Size Estimate = 56 Pages

Graphic Page Size Estimate = 45 Pages

Total Page Size Estimate = 101 Pages

Table I. Substituent Patterns for Substrates Examined in This Work

no. of atoms in substituents	aryl-to-alkyl bond type		
	primary Ar-CH ₂ R	secondary Ar-CH(R)R'	tertiary Ar-C(R ¹ R ²)R ³
C ₁			
C ₂			
C ₃			
C ₄			
C ₅			
C ₆			

Table II. MOMM-85 Calculated Steric Energies for Minimum Energy Conformations of Butylbenzene

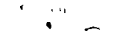


conformation	SE (kcal/mol) (ref)		
14aa	0		
14ag	1.85		
14ga	1.30		
14gs	2.02		

Table III. Number of Conformations of Various Isopropylbenzenes Based on Experiment and Conformational Analysis Predictions

compd	no. of conformations			obsd ^c
	predicted ^a			
	17 planar ^b	18 perpendicular ^b	19 gauche ^b	
isopropylbenzene (16)	1	1	1	1
1-isopropyl-3-methylbenzene (20)	2	1	2	2
1-ethyl-3-isopropylbenzene (21)				

^a Based on counting all possible molecular conformations having the specific substituent conformation depicted, but counting degenerate conformations only once. ^b This term refers to the relative position of the α -H and the plane of the aromatic ring. ^c Number of origin transitions observed by TOFMS. See text for additional discussion.

Table IV. Number of Conformations of Various *tert*-Butylbenzenes Based on Experiment and Conformational Analysis Predictions

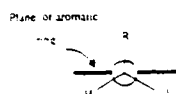
compd	no. of conformations			obsd ^a
	predicted ^a			
	 37 planar	 38 perpendicular	 39 gauche	
<i>tert</i> -butylbenzene (36)	1	1	1	1
1- <i>tert</i> -butyl-4-ethylbenzene (40)	1	2	2	1
1- <i>tert</i> -butyl-3-methylbenzene (42)	2	1	2	2
1,3-di- <i>tert</i> -butylbenzene (45)	3	2	6	3

^a Based on counting all possible molecular conformations having the specific substituent conformation depicted, but counting degenerate conformations only once. ^c Number of origin transitions observed by TOFMS. See text for additional discussion.

20

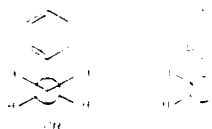
galley

STB16a



- 1a: R = CH₃
1b: R = CH₂CH₃

b



2

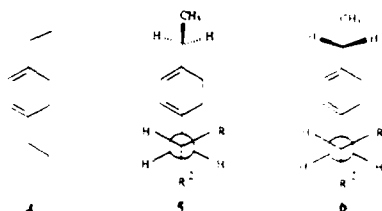
0°

3

19°

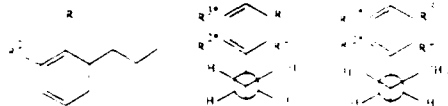
*Steric energy (kcal/mol) (rel)

c



- a: R¹ = H, R² = CH₃
b: R¹ = CH₃, R² = H

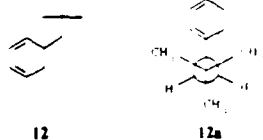
d



- 10: R¹ = H, R² = CH₃
11: R¹ = CH₃, R² = H

- a: all Rⁱ = H
b: R¹ = CH₃, R² = R³ = R⁴ = H
c: R¹ = CH₃, R² = R³ = R⁴ = H
d: R¹ = CH₃, R² = R³ = R⁴ = H
e: R¹ = CH₃, R² = R³ = R⁴ = H

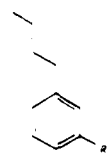
e



12

12a

f



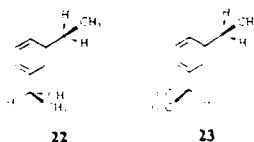
- 13: R = H
15: R = CH₃

STB16g



- 16: R = H
20: R = CH₃
21: R = CH₂CH₃

h



22

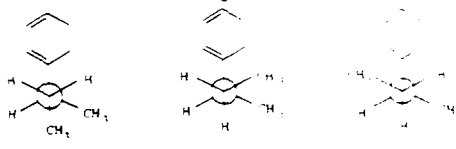
23

i



- 24: R¹ = R² = H
25: R¹ = CH₃, R² = H
26: R¹ = R² = CH₃

j



27

0.81°

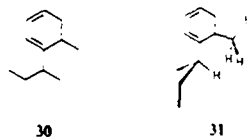
28

2.94°

29

*Steric Energy (kcal/mol) (rel)

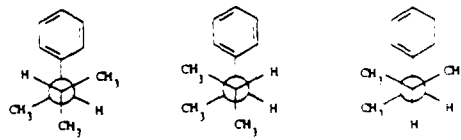
k



30

31

l



32

0°

33

0.95°

34

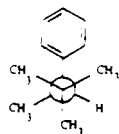
1.3°

*Steric energy (kcal/mol) (rel)

(21)

↓ 2.316 km

galla



35

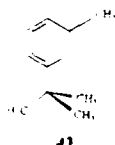
n



- 36 R' = R'' = H
40 R' = H; R'' = CH₂CH₃
42 R' = CH₃; R'' = H
45 R' = (CH₃)₂C; R'' = H

41

C

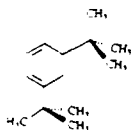


43

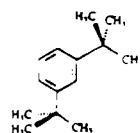


44

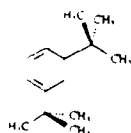
P



46



47



48

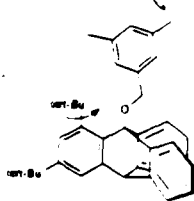
*Steric energy (kcal/mol) (rel.)

0.0

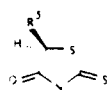
0.30

0.15

u



49

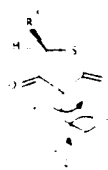


50



51

S



52

95

55

DL/1113/89/1

TECHNICAL REPORT DISTRIBUTION LIST, GENERAL

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Chemistry Division, Code 1113 800 North Quincy Street Arlington, VA 22217-5000	3	Dr. Ronald L. Atkins Chemistry Division (Code 385) Naval Weapons Center China Lake, CA 93555-6001	1
Commanding Officer Naval Weapons Support Center Attn: Dr. Bernard E. Douda Crane, IN 47522-5050	1	Chief of Naval Research Special Assistant for Marine Corps Matters Code 00MC 800 North Quincy Street Arlington, VA 22217-5000	1
Dr. Richard W. Drisko Naval Civil Engineering Laboratory Code L52 Port Hueneme, California 93043	1	Dr. Bernadette Eichinger Naval Ship Systems Engineering Station Code 053 Philadelphia Naval Base Philadelphia, PA 19112	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	2 <u>high</u> <u>quality</u>	Dr. Sachio Yamamoto Naval Ocean Systems Center Code 52 San Diego, CA 92152-5000	1
David Taylor Research Center Dr. Eugene C. Fischer Annapolis, MD 21402-5067	1	David Taylor Research Center Dr. Harold H. Singerman Annapolis, MD 21402-5067 ATTN: Code 283	1
Dr. James S. Murday Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1		